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MAGNETISM

Specific Features of the Electrical Resistance of Half-Metallic Ferromagnetic Alloys Co_2CrAl and Co_2CrGa

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Abstract—It has been shown by comparing the results of studying the electrical and magnetic properties of the half-metallic ferromagnetic Heusler alloys Co_2CrAl and Co_2CrGa with the calculations of their electronic structure that high values of the electrical resistivity ρ are caused by a disordered distribution of atoms over the sites of the $L2_1$ cubic structure, and the anomalous behavior of $\rho(T)$ is associated with the transformation of the electronic spectrum due to the ferromagnetic-to-paramagnetic transition.

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Half-metallic ferromagnetic Heusler alloys are characterized by the presence of an energy gap in their electronic spectrum at the Fermi level E_F of one of the subbands, which differ in the direction of the electron spins with respect to the magnetization vector [1]. Half-metallic ferromagnets are distinguished among other Heusler alloys by the fact that their spin polarization can reach a limiting value of ~100%. Owing to this reason, studying the physical properties of half-metallic ferromagnetic alloys as promising objects for possible use in spintronic devices has been recently of great interest. The energy gap in the half-metallic ferromagnetic alloys Co_2CrAl and Co_2CrGa under investigation is known to be formed at the Fermi level in the subband of electrons with spins oriented opposite to the magnetization vector (see, e.g., [1–6] and references therein). These alloys are ordered to form the crystal structure $L2_1$ of cubic symmetry. Their formula is X_2YZ, where X and Y are transition metals and Z is a Group III–V element of the Periodic Table, with the specific (shown in Fig. 1) filling of four sublattices of the fcc lattice by the atoms of different sorts.

As a rule, half-metallic ferromagnets exhibit high values of the resistivity ρ. For example, as is seen in Fig. 2, the residual resistivity of the Co_2CrAl and Co_2CrGa alloys is $\rho_0 \sim 1.5$ and 1.3 μΩ m, respectively. In addition, the $\rho(T)$ curves of these half-metallic ferromagnets near the Curie point T_C are characterized by pronounced features: a sign change of the resistance temperature coefficient of the Co_2CrAl alloy [2, 3] and a peak-type anomaly in Co_2CrGa [4]. The high values of ρ_0 and the negative resistance temperature coefficient of Co_2CrAl at $T < T_C$ were attributed in [5, 6] to the presence of a mixture of metallic and semiconductor phases in the samples. The structural heterogeneity of the samples was also associated in [5, 6] with a difference—almost by a factor of 2—between the experimentally measured and calculated magnetic moments of the ultimately ordered Co_2CrAl alloy. However, as was correctly mentioned in [2], the sign change of the resistance temperature coefficient near T_C in the absence of structural changes in this temper-

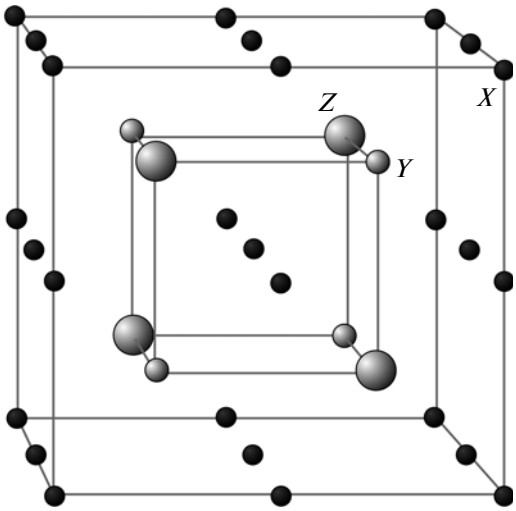

Fig. 1. Crystal structure of Co_2CrAl and Co_2CrGa half-metallic ferromagnets. The lattice is formed by four sublattices of three different types: the positions of type X (outer sublattice of black spheres) are occupied by Co, and the positions of types Y and Z (embedded sublattice of small and large gray spheres) are occupied by Cr and Al (Ga), respectively.

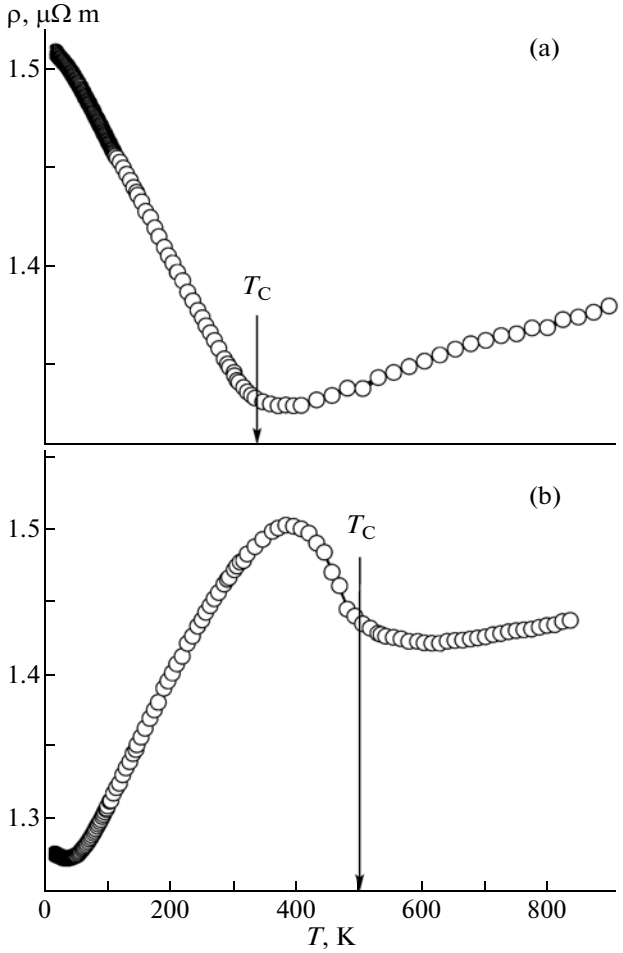

Fig. 2. Electrical resistivity of half-metallic ferromagnetic Heusler alloys: (a) Co_2CrAl and (b) Co_2CrGa.

ature range indicates another reason of the anomalous behavior of $\rho(T)$.

In [3, 4], the specific behavior of $\rho(T)$ in half-metallic ferromagnets was attributed to both the scattering mechanisms usually characterized by the relaxation time τ or the mean free path length $l = 1/\tau$ of conduction electrons and the specific electronic band structure of the alloys, i.e., the number n of charge carriers. Consequently, the conductivity $\sigma = 1/\rho$ in the simplest case is determined by the well-known relation

$$\sigma = \frac{ne^2\tau}{m^*}, \qquad (1)$$

where e is the absolute value of the electron charge and m^* is the effective mass of charge carriers. Consideration of the temperature dependence of the resistance of half-metallic ferromagnets takes into account two conduction channels for electrons with spins ($\uparrow$) along and ($\downarrow$) opposite to the magnetization vector. The conductivity $\sigma_\uparrow$ of the former channel for the spin-$\uparrow$ electrons has a usual form for ferromagnetic alloys. It is determined primarily by scattering of charge carriers by inhomogeneities of the magnetic subsystem and the crystal lattice, i.e., by the parameter τ in Eq. (1). The conductivity $\sigma_\downarrow$ of the latter channel (spin-$\downarrow$ electrons) largely depends on the parameters of the energy gap in the electronic spectrum; i.e., it is determined by the density of states $n_\downarrow \sim 0$. If the band gap is centered exactly at E_F and has the limiting depth in the ground state (at $T \sim 0$ K), the spin-$\downarrow$ charge carriers are almost absent and consequently $n_\downarrow \sim 0$. In this case, one should expect that the temperature dependence of $\sigma_\downarrow$ is of semiconductor type determined by the variation of the number of spin-$\downarrow$ charge carriers with temperature. Taking into account a rather high resistivity of half-metallic ferromagnets, the total conductivity should be described by the expression

$$\sigma = \sigma_\uparrow + \sigma_\downarrow \quad \text{or} \quad \rho = \frac{\rho_\uparrow\rho_\downarrow}{\rho_\uparrow + \rho_\downarrow}. \qquad (2)$$

Naturally, the band-gap contribution to the resistivity $\rho_\downarrow$ is shunted at low σ, i.e., when $\sigma_\uparrow \gg \sigma_\downarrow$. Consequently, according to [3, 4], the specific behavior of $\rho(T)$ of half-metallic ferromagnets is determined by the relation between the conductivities of two channels. When $\sigma_\uparrow$ is low and comparable with $\sigma_\downarrow$, a considerable role is played by the band-gap contribution to the total resistivity. As is known [1–6], the depth and width of the band gap of a half-metallic ferromagnet can vary considerably under the action of internal stress, structure distortions and especially as a result of disordering effects. As was shown in [2], a decrease in the magnitude of the magnetic moment of real Co_2CrAl samples as compared to the calculated value for the ideal ordered alloy can be caused by the presence of Co atoms in the positions of Cr and Al. This naturally leads to a decrease in the depth of the band gap in the electronic spectrum and, consequently, to a decrease in $\rho_\downarrow$. At the same time, the presence of atomic disorder results in an increase in both $\rho_\uparrow$ and the total resistivity of the alloy as compared to the ideal case. As was shown in [3], the presence of a feature in the electronic spectrum of Co_2CrAl half-metallic ferromagnet under investigation is indicated by the effect of magnetic ordering on ρ. At temperatures below T_C, we have

$$\rho = \rho_0 + cM^2, \qquad (3)$$

where the coefficient $c > 0$ [7]. Inclusion of the phonon contribution to the resistivity, which is described by the Bloch–Grüneisen function $\rho_{ph}(T)$, can explain the minimum of $\rho(T)$ of Co_2CrAl observed near T_C (see Fig. 2).

As is seen in Fig. 2, the $\rho(T)$ curve of Co_2CrGa half-metallic ferromagnet is most complicated. It resembles the one of manganese near the Néel point and is explained in [8] by superposition of the phonon and magnon contributions to resistivity, when a linear increase in $\rho_{ph}(T)$ is superimposed by a sharp decrease of the magnetic contribution owing to disappearance

of spontaneous magnetization. As was derived in [8], in the mean-field approximation,

$$\rho(T) = \rho_{ph}(T) + \rho_m(T) = \alpha T + \beta[1 - M_s^2(T)] + \gamma M_s^2(T) T. \quad (4)$$

According to [4], similar situation takes place in Co_2CrGa half-metallic ferromagnet. The spontaneous magnetization $M_s \longrightarrow 0$ vanishes at $T \longrightarrow T_C$. This leads to disappearance of the gap near E_F for the subband of spin-↓ electrons and, consequently, to a sharp decrease in the term $\rho_\downarrow$. With a further increase in temperature, $\rho_\downarrow$ levels off and the temperature behavior of the resistivity at $T > T_C$ is determined by the contribution of $\rho_{ph}(T)$ alone. The question of the validity of this approximation, which holds only at a high resistivity $\rho_\uparrow$, remains unclear. It should be also taken into account that the values of the magnetic moment calculated for the fully ordered alloy and measured in real samples nearly coincide [9, 10].

To clarify the reasons leading to a higher value of the resistivity of Co_2CrGa half-metallic ferromagnet under the condition of the preserved band gap in the electronic spectrum near E_F we calculated the electronic band structure of Co_2CrGa taking into account distortions of the ordered arrangement of individual atoms in the crystal lattice sites. The calculation of the electronic band structure was performed using the tight-binding linear muffin-tin orbitals atomic sphere approximation (Stuttgart TB-LMTO-ASA program, Version 47) [11]. The orbital basis consisted of the orbitals corresponding to the 4*s*, 4*p*, and 3*d* states of Co and Cr ions and the 4*s*, 4*p*, and 4*d* states of Ga ions.

Figure 3 shows the total and partial Cr-3*d* and Co-3*d* electron densities of states of the Co_2CrGa half-metallic ferromagnet in the fully ordered state (Fig. 3a) and in the supercell with the single mutual substitution Cr ⟷ Ga (positions $Y \longleftrightarrow Z$) (Fig. 3b) and the single mutual substitution Co ⟷ Cr (positions $X \longleftrightarrow Y$) (Fig. 3c). The electron density of states of the ordered alloy in the energy range near the Fermi level consists of several bands with a large number of sharp peaks formed almost entirely by the 3*d* subbands of cobalt and chromium. The calculated energy spectra reproduce a wide band gap in the density of states of spin-↓ electrons formed almost entirely by 3*d* states of Co, which also hold for Co_2CrAl [3]. At the same time, high values of the density of states of electrons with the opposite spin are determined by both the Cr-3*d* (darkened area) and Co-3*d* states. The choice of a particular type of substitutional defects is based on the experimental data on neutron scattering [10], which indicate almost perfect occupation of the position *X* by Co atoms and a lower occupation of the position *Z* by Ga atoms.

The calculations for the alloys with the mutual substitutions Cr ⟷ Ga were performed for the supercells with four formula units, which allowed us to estimate

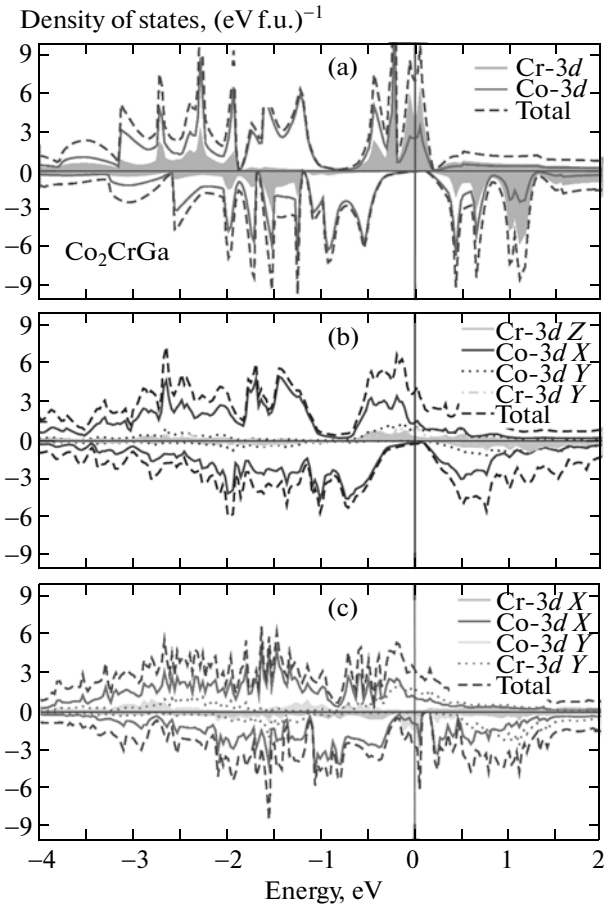

Fig. 3. Total and partial 3*d* densities of states for Co_2CrGa (a) in the fully ordered state and (b, c) in the supercell with (b) the single mutual substitution Cr ⟷ Ga and (c) the single mutual substitution Co ⟷ Cr. The notation of the density of states of the disordered alloys includes the type of atomic positions (*X*, *Y*, or *Z*). The Fermi level is located at zero.

the effect of this type of defects at a minimum possible distance between the substituted atoms. The densities of states shown in Fig. 3b indicate that the profile of the density of states in the case of the single substitution Ga ⟷ Cr remains almost unchanged for both spins and the energy gap for spin-↓ electrons persists at the emergence of an insignificant electron density of states. According to the analysis of the partial 3*d* densities of states of Cr and Co, the cause of such an insignificant effect of the substitutions Cr ⟷ Ga on the band gap is preserving of the profile and position of the Co-3*d* states, which form the band gap. A similar form of the spectrum with the preserved energy band gap was obtained in the calculations for the supercells with double Cr ⟷ Ga substitutions (two of four atoms substitute the ions from another sublattice not shown in Fig. 1). In this work we also performed calculations for the supercells with the substitutions $X \longleftrightarrow Y$ and $X \longleftrightarrow Z$. It should be mentioned once more that the experimental data on neutron scattering [10] do not

confirm substitutions involving the cobalt sublattice. Figure 3c presents the calculation results for the alloys with the single substitution Cr ⟷ Ga (the type $X \longleftrightarrow Y$); the spectrum with a similar character was found also for the $X \longleftrightarrow Z$ and double substitutions. As is seen in Fig. 3c, in this case, the band gap at the Fermi level is replaced by a high electron density of states owing to the 3*d* states of cobalt ions in the positions *X* and *Y* (shown by the darkened area), which obviously contradicts with the available experimental data [4, 9, 10].

Self-consistent calculation for the unit cell yields the following values of the magnetic moments for Co_2CrGa half-metallic ferromagnet: the total moment is $3.01\mu_B$, the moments at Co, Cr, and Ga are 0.79, 1.50, and $-0.07\mu_B$, respectively, in good agreement with the experimental data and earlier ab initio calculations (see, e.g., [9]). For both cases of mutual substitutions Cr ⟷ Ga, the total magnetic moment per formula unit does not change being 3.03 (3.07) μ_B for the single (double) substitution, the moments of Co and Ga remain almost unchanged, 0.78 (0.79) and −0.08 (−0.07) μ_B, respectively, whereas chromium ions are divided into pairs with magnetic moments of 1.38 (1.35) and 1.72 (1.76) μ_B. Additional calculations of the substitutions involving cobalt sublattices (the types $X \longleftrightarrow Y$ and $X \longleftrightarrow Z$) indicate that such disturbances of the order drastically change the above picture leading to a change in the total magnetic moment to 4.71 or 2.40 μ_B and a high density of states emerges instead of the band gap at the Fermi level, which clearly disagrees with all available experimental data.

Thus, distortion of the ordered arrangement of atoms in their sites in the crystal lattice can be the main cause of a high resistivity of the half-metallic ferromagnets and, consequently, this particular atomic disordering is the main cause of the observed features of $\rho(T)$. A difference in the behavior of the electrical and magnetic properties of the alloys under consideration is that Co_2CrGa basically exhibits disordering in the Cr and Ga sublattices, whereas such disordering in Co_2CrAl takes place in all sublattices. Therefore, in our opinion, the alloys Co_2CrGa is preferred for the use in spintronic devices.

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